New Coordinative Compounds of Mn(II) and Cu(II) Using as Ligand N-hydroxy-succinimide

MIHAELA-DANA TUTULEA[1]*, IOAN ROSCA[1], IGOR CRETESCU[1], ADRIAN CAILEAN[1], IONUT LUCIAN BISTRICIANU[2]

[1]"Gh. Asachi" Technical University, Faculty of Chemical Engineering and Environmental Protection, Chemical Engineering Department, 73 D. Mangeron, 700050, Iasi, Romania

[2]"Gh. Asachi" Technical University, Faculty of Mechanical Engineering, 67 D. Mangeron, 700050, Iasi, Romania

This paper deals with synthesis and characterization of new coordinative compounds of Mn(II) and Cu(II) using as ligand N-hydroxy-succinimide. Synthesis of the new coordinative compounds was carried out at room temperature, under 45 minutes stirring of two 10^{-2} M solutions of each reagent (Ligand N-hydroxy-succinimide and respectively Mn(II) or Cu(II) ions) in molar ratio 1:1 and corresponding 2:1 (ligand : central atom). The brown crystals for copper (II) complexes and orange to yellow for manganese (II) complexes were obtained by slow evaporation at room temperature. The characterization of obtained complex compounds was performed using the EDAX elemental chemical analysis, thermogravimetry, IR absorption spectroscopy, ESR spectroscopy and X-ray diffraction. To determine the molar ratio ligand : central atom were used methods as pH-metry, conductometry and the UV-VIS absorption spectroscopy. The stability constants for new obtained compounds, in aqueous medium, were determined using molar ratio method (J.H.Yoe and A.L.Jones). The new coordinative compounds crystallize in triclinic system.

Keywords: coordinative compounds of Cu (II), Mn (II), thermal stability

Complex combinations research field includes a wide range of theoretical investigations with various practical applications, attracting a large number of researchers. It is well known particularly important role of complex combinations in the development of quantitative and qualitative analysis methods. Some metal ions, especially iron, copper and manganese are involved in cells energetic metabolism. These ions function as components of metalloenzymes that take part in reduction reactions [1].

The ability of copper (II) and manganese (II) ions to bind both hard and soft donor ligands allows their coordination chemistry to include a variety of geometrical structures and oxidation states corresponding to different reactivity, ranging from biological systems to organometallic chemistry [2].

N-hydroxy-succinimide is a bidentate ligand, with application in organic chemistry and biochemistry, being used as activating agent for carboxylic acids.

Metal complexes containing N-hydroxy-succinimide ligand were the subject of many research interests, due their rich coordination chemistry and applicability in different areas [3]. This ligand is very popular due to their applications as: the immobilization of human serum albumin, protein and peptides, the synthesis of different acids, solid-state additive, antibodies, and pharmaceutical drugs, the obtaining of quantum dots crystals [4 - 7].

In order to obtain new coordination compounds with applicability in analytical chemistry of manganese and of copper ions respectively , the authors have synthesized and studied the Mn(II) and Cu(II) complexes, using as ligand N-hydroxy-succinimide in molar ratio ligand : central atom 1:1 and 2:1 respectively.

The studies of these compounds were performed applying the EDAX elemental chemical analysis, thermogravimetry, IR absorption spectroscopy, ESR spectroscopy and X-ray diffraction.

* *email: dtutulea@ch.tuiasi.ro*; *Tel.: 0724006847*

New coordination compounds present a high thermal resistance up to 170°C, after that the compounds are decomposed in one or three phases. Based on the thermogravimetric data, the reaction order and the activation energy were calculated.

From infrared spectra result that the central atoms Mn(II) and Cu(II) respectively, binds to oxygen atoms from $>C=O$ and $(H)-O-N<$ groups.

Based on the XRD investigation, all studied compounds crystallize in the triclinic system.

Experimental part

The used reagents were provided from Merck and were used without any purification in 10^{-2} mol/L solutions of $MnCl_2 \cdot 4H_2O$, $CuCl_2 \cdot 2H_2O$, and respectively of N-hydroxy-succinimide.

Synthesis of the new coordinative compounds was carried out into a glass vessel of 250 mL, at room temperature, under 45 min stirring of two 10^{-2} M solutions of each reagent (Ligand N-hydroxy-succinimide and respectively Mn(II) or Cu(II) ions) in molar ratio 1:1 and corresponding 2:1 (ligand : central atom).

The brown crystals for copper (II) complexes and orange to yellow for manganese (II) complexes were obtained by slow evaporation at room temperature.

It has been demonstrated that the Cl^- anion is placed in the exterior sphere of the complexes $[MnL \cdot 2H_2O]Cl$ and respectively $[CuL \cdot 2H_2O]Cl$, using the titration of their solutions with $AgNO_3$.

The obtained solid compounds were purified by re-crystallizing from concentrated solutions, and were dried at room temperature in dessicator with calcium chloride.

EDAX elemental chemical analysis was performed using EDAZ TSL AMETEK with an aluminum base plate.

The method applied to study the complex formation in solution was "molar ratio" method [8] and to determine the stability constants was used Harvey-Manning method [9].

For the specific electric conductibility of the solutions, a Radelkis –Budapest OK 109 conductometer was used. The *p*H measurements were carried out using a pH-meter type HACH ONE. For the spectral values determination, in visible domain, a Perkin-Elmer Spectrum 100 spectrophotometer was used.

IR spectra were recorded on a FTIR 660 Plus spectrometer using KBr pellets [10] in the 4000–200 cm^{-1} range.

The thermal analysis and parameter determination of thermal decomposition reactions were carried out using the derivatograms recorded by a Q1500D (MOM Budapesta) derivatograph.

Complex samples, weighing 100 mg each, were heated with a 10°C/min speed [11] to 1000°C temperatures, and were recorded thermogravimetric (TG), derivative thermogravimetric (DTG) and the variation of temperature (T) curves represented in figure 7.

ESR spectra of the studied compounds were carried out using an IFA Bucharest spectrometer using diphenyl picryl hydrozyl (DPPH) as reference and a 3216.9 Gauss magnetic field, corresponding to the standard sample center spectrum with a frequency of 9030 MHz.

Based on double integration graphic methods were calculated the number of electrons corresponding to a gram of each compound studied, respectively a central atom, and the g spectroscopic splitting factor [12].

It was used a X'PERT Pro MRD Panalytical diffractometer to record X-ray diffractograms, with a Cu anode, 45 kV voltage, intensity of 40 mA, a nickel filter and K_α1: 1.54 Å radiation, in the 2θ = 0-100°C angular range. Samples were mortared in order to obtain a homogeneous powder. The dust was attached in a thin layer to a microscope and the parameters of elemental cells were determined.

Results and discussions

Obtaining of Mn(II) and Cu(II) complexes in solution

New coordinative compounds were noted:

N-hydroxy-succinimide – was noted HL;

$[MnL\cdot 2H_2O]Cl$ - complex derived from interaction between $MnCl_2$ and N-hydroxy-succinimide in molar ratio 1:1;

MnL_2 - complex derived from interaction between $MnCl_2$ and N-hydroxy-succinimide in molar ratio 1:2;

$[CuL\cdot 2H_2O]Cl$ - complex derived from interaction between $CuCl_2$ and N-hydroxy-succinimide in molar ratio 1:1;

CuL_2 - complex derived from interaction between $CuCl_2$ and N-hydroxy-succinimide in molar ratio 1:2.

From the graphic representations of conductivity - L/Cu^{2+} (fig.1), it results that two coordinative compounds were formed corresponding to molar ratio 1:1 and 2:1 L/M respectively, due to the interaction between Cu^{2+} with HL ligand.

Studying the experimental data using "molar ratio" method in pH-metry and conductivity variant, it can be observed that were obtained curves with graph slope changing at molar ratio ligand : central atom 1:1 and 2:1.

From the graphic representations resulted that when it is formed the maximum quantity of the complex the graph slope changes.

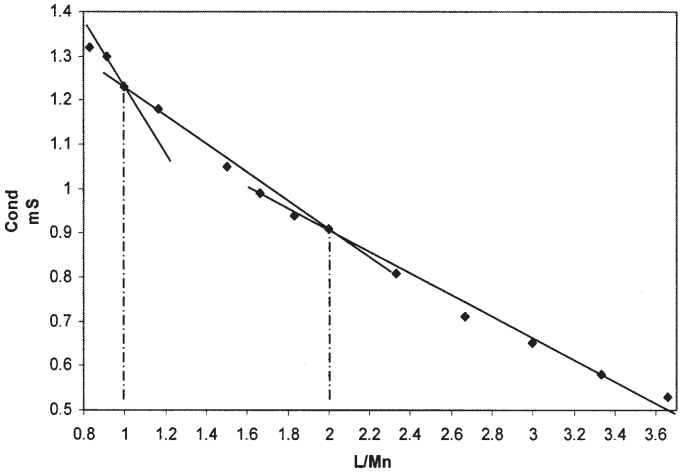

Fig. 1. The curve representing conductivity values of the solutions HL – $MnCl_2$, versus the molar ratio L/Mn

Experimental data showed that the new complexes were formed in aqueous medium in molar ratio 1:1 and 2:1, respectively.

The values of the stability constants for the new obtained compounds are: $\beta_1 = 2.66\cdot 10^5$ L/mol for $[CuL\cdot 2H_2O]Cl$, and $\beta_2 = 9.38\cdot 10^8$ L/mol, for CuL_2.

Solid - state analysis of the $[MnL\cdot 2H_2O]Cl$, MnL_2, $[CuL\cdot 2H_2O]Cl$ and CuL_2 *coordination compounds*

EDAX elemental chemical analysis

EDAX elemental chemical analysis of the studied compounds is presented in table 1, establishing the following formula: $[Cu(C_4H_4NO_3)\cdot 2H_2O]Cl$, $[Cu(C_4H_4NO_3)_2]$, $[Mn(C_4H_4NO_3)\cdot 2H_2O]$, $[Mn(C_4H_4NO_3)_2]$.

It can be noticed that between the calculated values and the experimental data with a ±0.28% error was a good correspondence.

Infrared spectroscopy

In order to determine the way of binding metal atoms by the ligand, the IR spectra, in the 4000-200 cm^{-1} range, for both free ligand and the obtained complexes, were recorded.

IR spectra of all the compounds were recorded in the 200-700 cm^{-1} range with the aim to identify M-O frequency. The weak bands observed in the 437-444 cm^{-1} region could be attributed to the Cu-O vibration from $[CuL\cdot 2H_2O]Cl$ complex. Also, the bands observed in the 445 cm^{-1} region could be attributed to the Cu-O vibration from CuL_2 complex. Concerning the IR spectra of manganese complexes, it is presented a Mn-O frequency at 431-458 cm^{-1} range in the $[MnL\cdot 2H_2O]Cl$, and a Mn-O frequency at 450 cm^{-1} range for MnL_2, respectively. These results were in agreement with literature values [13 - 15].

Analyzing the IR spectra of the complexes it was observed that they contain a number of new bands compared to the ligand spectrum. Thus, in the 3370-3400 cm^{-1} range, complexes $[CuL\cdot 2H_2O]Cl$ and $[MnL\cdot 2H_2O]Cl$ respectively, presented a medium intensity band assigned to OH stretching vibration. Hence, it can be concluded that

Complex	C		H		N		Cl		M	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
$[CuL\cdot 2H_2O]Cl$	19.12	19.18	3.18	3.12	5.58	5.68	14.12	14.19	26.11	26.09
CuL_2	32.70	32.76	2.72	2.65	9.54	9.63	-	-	22.32	22.28
$[MnL\cdot 2H_2O]Cl$	19.96	20.04	3.32	3.41	5.82	5.91	14.74	17.81	22.85	22.76
MnL_2	33.92	33.87	2.82	2.93	9.89	9.93	-	-	19.41	19.48

Table 1
ELEMENTAL CHEMICAL COMPOSITION OF STUDIED COMPOUNDS (%)

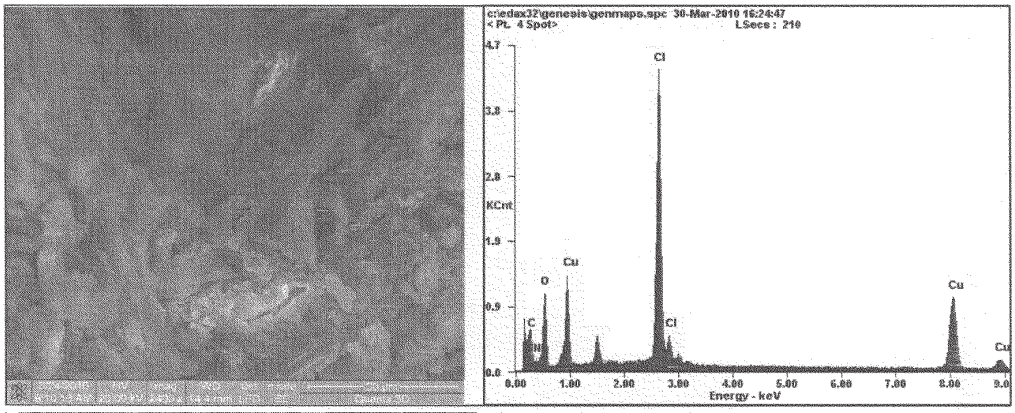

Fig. 2. SEM-EDX spectrum for characterizing the chemical composition of the complex $[CuL \cdot 2H_2O]Cl$

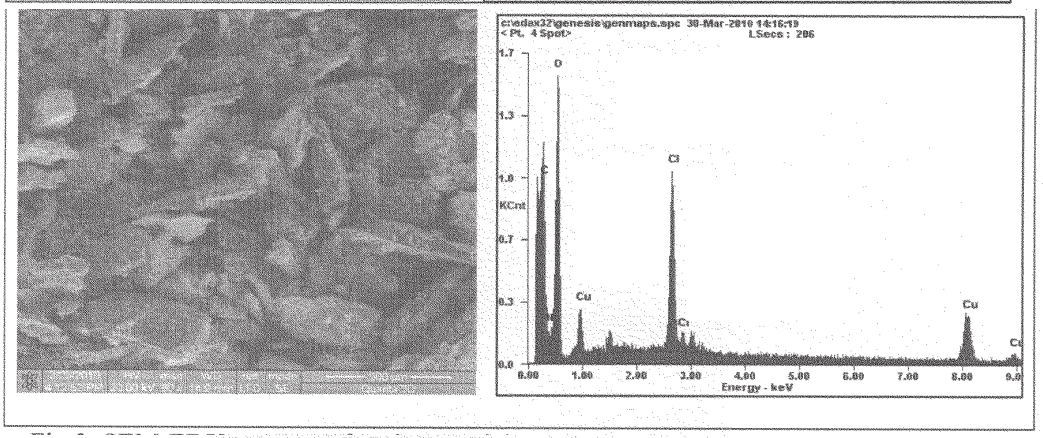

Fig. 3. SEM-EDX spectrum for characterizing the chemical composition of the complex CuL_2O

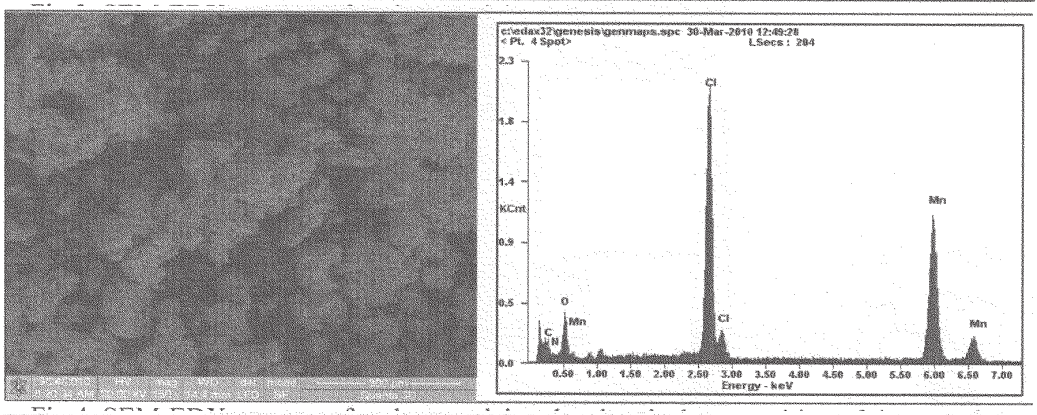

Fig.4. SEM-EDX spectrum for characterizing the chemical composition of the complex $[MnL \cdot 2H_2O]Cl$

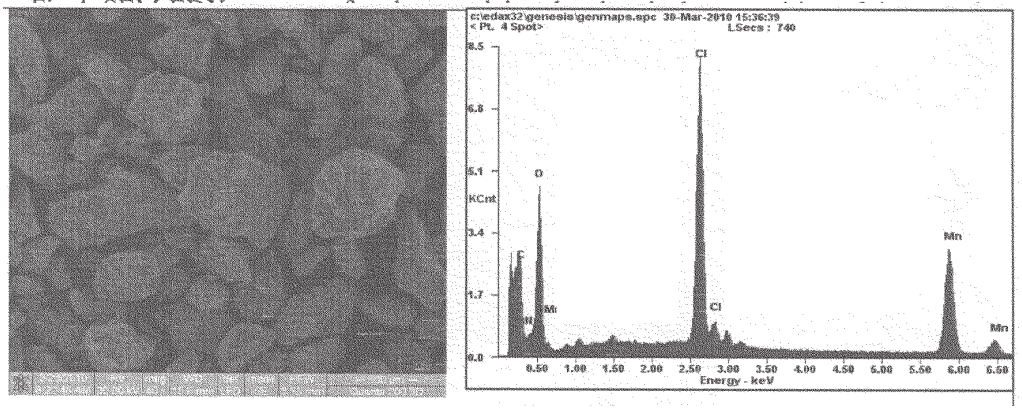

Fig.5. SEM-EDX spectrum for characterizing the chemical composition of the complex MnL_2

these compounds contain water, in accordance with elemental chemical analysis (table 1).

Absorption band at 1715 cm^{-1} issued in the ligand spectrum, corresponds to the stretching vibration of the C=O group [16]. This stretching vibration appears in the $[CuL \cdot 2H_2O]Cl$ and $[MnL \cdot 2H_2O]Cl$ complexes spectra, as symmetric and asymmetric vibrations [17]. In case of CuL_2, the asymmetric vibration disappears. Harmonic vibration corresponding to the carbonyl group appears as a low intensity band with peak at 3430 cm^{-1}. This band can be easily confused with the band corresponding to the OH group, also found in the structure of the studied coordinative compounds.

In the infrared spectrum low - frequency (400 - 1500 cm^{-1}) appears bands corresponding to stretching vibration of C-C, C-N bonds [18] and to various deformation vibrations bonds.

Simple bonds as C-C, C-O and C-N were strong vibrations coupled with each other to engender a multitude of bands, so-called skeleton vibration of the molecule.

The ligand presents, in the 1310-1280 cm^{-1} range, a band that corresponds to the N-OH bond, while in the studied

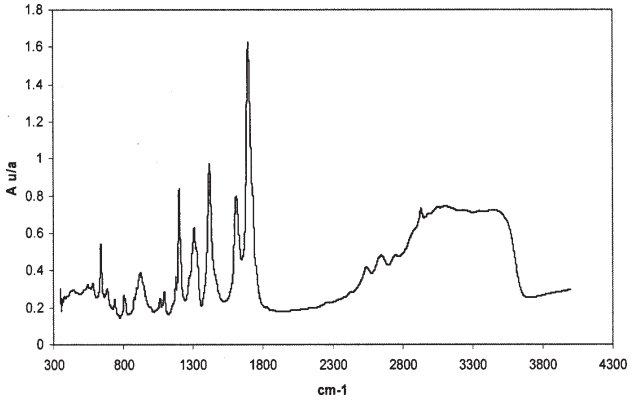

Fig.6. IR spectrum of $[CuL{\cdot}2H_2O]Cl$ complex

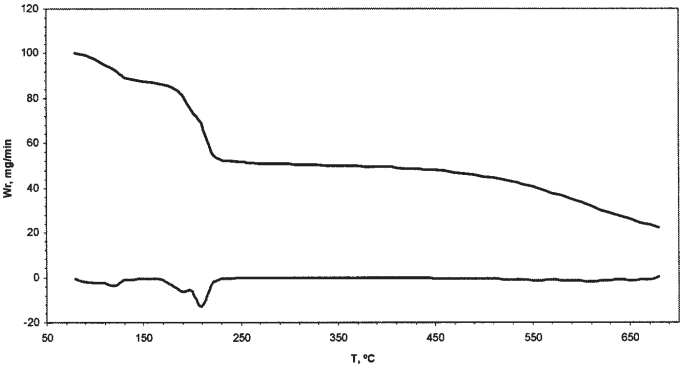

Fig.7. $[CuL{\cdot}2H_2O]Cl$ thermogram

compounds disappears, which could demonstrate that the coordination occurs through OH group.

It should be noted from the IR spectra that the coordination of central atoms was achieved by replacing the hydrogen atom from H-O-N and by coordination with oxygen atom from >C=O.

Coordinated water molecules by the central atoms of the studied compounds Cu←OH_2 and Mn←OH_2 presents symmetric and asymmetric stretch vibrations at 3395-3300 cm^{-1}, 3379-3300 cm^{-1} respectively and deformation vibrations at 1620-1625 cm^{-1} respectively at 1600-1610 cm^{-1} in agreement with values indicated in literature [19].

Thermal analysis

Analysis of TG-DTG curves (fig. 7) showed that the thermal decomposition of the complex $[CuL{\cdot}2H_2O]Cl$ recorded three distinct areas. The first stage corresponds to water loss at temperatures below 150°C and the thermal decomposition carries on two sequences in the range of temperatures of 160-680°C.

From the CuL_2 and $[MnL{\cdot}2H_2O]Cl$ thermograms, it can be observed that the thermal decomposition of the complexes started at 180°C.

Differential thermal analysis of the $[CuL{\cdot}2H_2O]Cl$ complex showed one well-defined endothermic peak with maximum at 220°C, and CuL_2 complex presented a peak at 230°C.

The total weight loss was almost constant in the last stage of decomposition, so in the first stage the losses were higher, the second stage were lower.

The thermal decomposition of the MnL_2 complex starts at temperature of 280°C and ends at 590°C, leading to the formation of a residual product in a 27.25% rate.

In order to calculate the activation energy and the reaction order was used Freeman-Carroll method [20] and the obtained values were presented in table 3.

The activation energy for the first stage varies widely from one complex to another, from 143.6 kJ / mol for $[MnL{\cdot}2H_2O]Cl$ to 79.8 kJ / mol for MnL_2.

The thermal decomposition global reactions of the studied coordinative compound could be described as follow:

$$[Mn(C_4H_4NO_3){\cdot}2H_2O]Cl \rightarrow Mn_3O_4 + \text{volatile}$$
$$[Mn(C_4H_4NO_3)_2] \rightarrow Mn_3O_4 + \text{volatile}$$
$$[Cu(C_4H_4NO_3){\cdot}2H_2O]Cl \rightarrow CuO + \text{volatile}$$
$$[Cu(C_4H_4NO_3)_2] \rightarrow CuO + \text{volatile}$$

Table 2
CHARACTERISTIC BANDS IN IR (cm^{-1}) OF LIGAND AND THE STUDIED COMPLEXES

Complex	ν_{N-OH}	$\nu_{C=O}$		ν_{H2O}	N_{M-O}
		Asim.	Sim.		
HL	1280	1715			-
$[CuL{\cdot}2H_2O]Cl$	-	1603	1697	3395-3300	437
CuL_2	-	-	1694	-	445
$[MnL{\cdot}2H_2O]Cl$	-	1630	1702	3379-3300	431
MnL_2	-	-	1696	-	450

Table 3
CHARACTERISTIC TEMPERATURES OF THE THERMAL DECOMPOSITION, REACTION ORDER AND ACTIVATION ENERGIES (kJ/mol) OF THE LIGAND AND THE STUDIED COMPLEXES

Complex	Stage I				Stage II				Stage III			
	Ti, °C	Tf, °C	n	E	Ti, °C	Tf, °C	n	E	Ti, °C	Tf, °C	n	E
HL	160	260	0.93	221.7	270	530	0.99	116	-	-	-	-
$[CuL{\cdot}2H_2O]Cl$	80	150	0.98	96.7	160	240	1.34	134.5	250	680	0.74	95.5
CuL_2	180	360	1.37	96.1	-	-	-	-	-	-	-	-
$[MnL{\cdot}2H_2O]Cl$	50	170	1.5	143.6	180	320	1.09	155.4	330	660	0.34	160.9
MnL_2	280	590	0.76	79.8	-	-	-	-	-	-	-	-

Table 4

TVALUES OF THE SPECTROSCOPIC SPLITTING FACTOR, INTENSITY OF THE MAGNETIC FIELD CORRESPONDING TO THE SAMPLE SPECTRUM CENTER AND ODD ELECTRON NUMBER OF THE CENTRAL ATOM FOR Mn(II) AND Cu(II)

Complex	g	H_x	Odd electron number/central atom
$[MnL{\cdot}2H_2O]Cl$	2.0285	3351.2	4.92
MnL_2	2.0270	3353.6	4.89
$[CuL{\cdot}2H_2O]Cl$	2.0127	3230.6	0.86
CuL_2	2.0118	3229.2	0.83

Table 5

ELEMENTAL CELL PARAMETERS OF THE OBTAINED COMPLEXES

Elemental cell parameters	Obtained values			
	$[CuL{\cdot}2H_2O]Cl$	CuL_2	$[MnL{\cdot}2H_2O]Cl$	MnL_2
a (Å)	5.254(6)	7.99(4)	7.53(2)	10.70(2)
b (Å)	6.352(8)	9.61(7)	8.50(3)	11.62(2)
c (Å)	13.75(2)	12.67(3)	10.843(9)	15.08(3)
α	69.37(8)°	71.4(5)°	79.7(2)°	52.4(1)
β	74.4(2)°	91.6(9)°	82.0(3)°	45.7(1)°
γ	112.40(6)°	137.4(3)°	140.2(1)°	32.52(6)°
$V/10^6$ pm^3	351.49640	591.25530	393.73770	720.29870

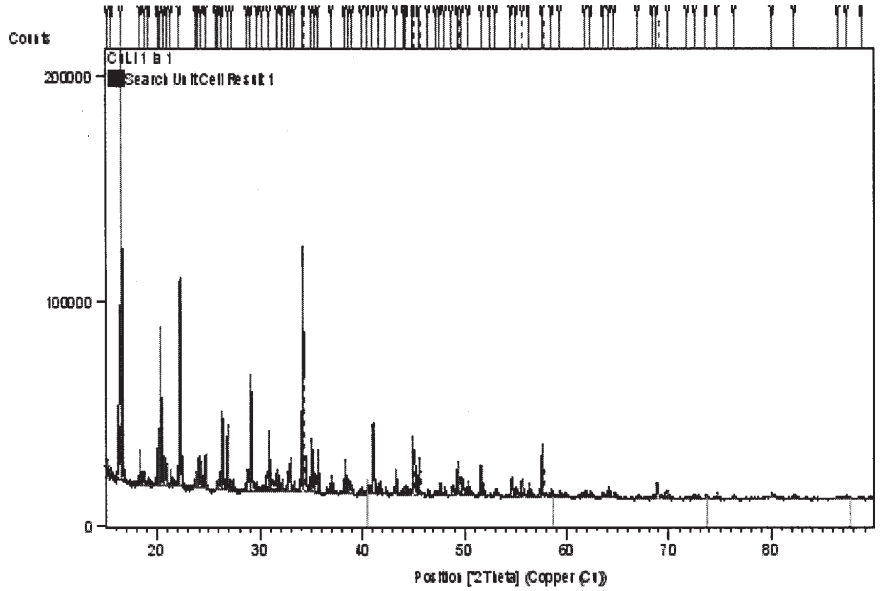

Fig. 8. $[CuL{\cdot}2H_2O]Cl$ complex diffractogram

Based on thermal decomposition reactions, the theoretical rates of volatile loss were calculated.

As it is known [19], the thermal decomposition reactions are disfavored by the transport of volatile compounds through the heating solid layer and the final products are in general the metallic oxides corresponding to the metallic ion involved in the coordination process. As it can be observed for all prepared coordinative compounds, the final solid products were identified as CuO and respectively Mn_3O_4. These results were in concordance with the literature data [21, 22].

ESR spectra

Based on ESR spectra, all obtained complexes are paramagnetic, with a maximum number of impair electrons of the central atoms. The spectroscopic splitting factor value was higher than that of the free electron, which is in correlation with ligands arrangement around the central atom, as it was also mentioned by other researchers [23, 24].

Also according to the ESR spectra, the number of impair electrons remains constant for the same central atom in all obtained coordinative compounds (table 4).

X-ray diffraction

Analyzing N-hydroxy-succinimide ligand diffractogram (fig. 8), the crystalline structure, was pointed out, allowing to establish a triclinic symmetry, with the elemental cell parameters: a = 6.82(1) Å, b = 8.49(1) Å, c = 14.14(3) Å, α = 85.1°, β = 107.1(2)°, γ = 58.29(9)°, $V/10^6$ = 636.05630 pm^3.

Based on the diffractograms of the studied complexes, a high crystalline degree was observed, the elemental cell parameters being presented in table 5.

The complexes formation occurs with increasing of the ligand packing degree. Based on this observation, the volume for elemental cell of the complexes was lower than for the ligand, due to the coordination and the hydrogen bonds formation between water molecules and the carbonyl group from the ligand.

Comparing difractograms of the complexes with that of the ligand it can be noticed that the ligand has been completely consumed in the reaction of formation of the respective complexes. This affirmation is based on the lack of ligand characteristic peaks in the diffractograms of the new obtained coordinative compounds.

The crystalline structure of the coordinative compounds was pointed out also by SEM spectra.

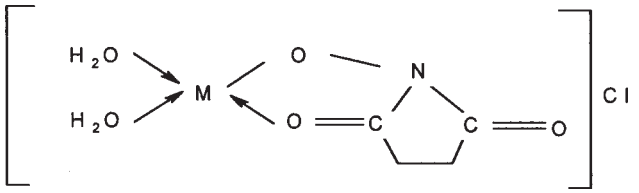

Fig.9. The structural formula of $[M(C_4H_4NO_3)\cdot 2H_2O]Cl$, M = Mn(II), Cu(II)

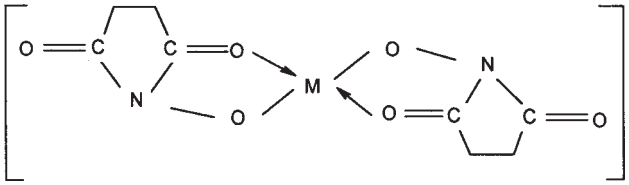

Fig.10. The structural formula of $[M(C_4H_4NO_3)_2]$, M = Mn(II), Cu(II)

In conclusion we can say that each central atom of the obtained coordinative compounds is tetracoordinated.

In case of $[MnL\cdot 2H_2O]Cl$ and $[CuL\cdot 2H_2O]Cl$ complexes, the central atom Mn(II) and Cu(II) respectively, bind to an oxygen atom from (H)O-N< group by the hydrogen substitution from the carbonyl group M←O=C< , forming stable cycles of five atoms. These central atoms were also bound by two water molecules and the tetracoordination arrangement was achieved.

CuL_2 and MnL_2 complexes have central atoms coordinated only by hydrogen atoms resulted from N-hydroxy-succinimide in the same manner as $[MnL\cdot 2H_2O]Cl$ and $[CuL\cdot 2H_2O]Cl$ respectively, and so being accomplished the tetracoordination arrangement.

Processing the ESR spectra of the studied complexes it results that the central atoms Mn(II) and Cu(II) present an external electronic structure $3d^5 4s^0 4p^0$, and $3d^9 4s^0 4p^0$ respectively, which means that the four bonds of these central atoms are achieved by hybrid sp^3 orbitals, directed according to the tetrahedron axis. This means that the structural formula of the obtained complexes could be described as is presented in figure 9, 10. However, for Cu(II) atom the ligand disposal could be according to square plan geometry, as were mentioned other previous papers [25].

Conclusions

New coordinative compounds of Mn(II) and Cu(II) ions based on the N-hydroxy-succinimide as ligand, were synthesized and characterized, corresponding to the molar ratio central atom : ligand 1:1 and respectively 1:2.

The studies in the liquid phase were carried out by pH-metry, conductometry and UV-VIS spectroscopy, determining the combination molar ratio and stability constants for each obtained coordinative compound.

The studies of the solid phase were performed applying modern methods as EDAX – elemental chemical analysis, thermal analysis, ESR and IR spectroscopy, and X-ray diffraction.

The crystalline structure of the obtained coordinative compounds for both Mn(II) and Cu(II) ions corresponding to the triclinic system was emphasized.

The complexation reactions of the Mn(II) and Cu(II) ions, using as ligand N-hydroxy-succinimide can be used in the analytical chemistry.

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